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Study on flotation tailings of Kaolinite-type pyrite when used as cement admixture and concrete admixture

Zheng Guo[1], Qiming Feng [1, 2*], Weiqing Wang [2], Yang Huang [2], Jie Deng [3], Zhonghui Xu[2]

[1.] School of Environment and Resource, Southwest University of Science and Technology, Mianyang, Sichuan 621010, PR China
[2.] Key Laboratory of Solid Waste Treatment and Resource Recycle Ministry of Education, Southwest University of Science and Technology, Mianyang, Sichuan 621010, PR China
[3.] Key Laboratory of Vanadium-titanium Magnetite Comprehensive Utilization, Ministry of Land and Resources, Chengdu, Sichuan 610000, PR China

Abstract

In Southwest China, the pyrite resources are very rich and the proven reserves of pyrite ranks first in the country. In the past 50 years of mining and processing, hundreds of millions of tons of tailings have been produced. However, the tailings have not been used effectively as yet, causing adverse effects to the local ecological environment. Therefore, according to the characteristics of the tailings, this article has studied on the pozzolanic activity of the tailings when used as cement admixture and the optimal amount of the tailings when used as concrete admixture. The results show that, being calcined on appropriate temperature and ground to certain fineness, the tailings will be provided with high pozzolanic activity. The activity index is up to 120%, so the tailings can be used as fine cement admixture and high-performance concrete admixture. The concrete will be provided with the highest compressive strength and still have good workability when the tailings replace cement for 20% by weight. The treatment method which gives a new approach for the efficient utilization of the tailings features simple production process, low energy consumption, no secondary pollution and high consumption of the tailings.

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Keywords: Kaolinite-type pyrite; Flotation tailings; Activity index; Cement admixture; Concrete admixture

* Corresponding author. Tel.: +86 13989291652
E-mail address: E-mail: 1252138465@qq.com.

1. Introduction

In Southwest China, there is a large number of sedimentary pyrite resources which has been found at the border region of Sichuan, Yunnan and Guizhou [1,2]. The explored reserves which accounts for 30% of the countrywide

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gross is no less than 6 billion tons. The pyrite occurs within the sedimentary kaolinite clay with the proportion that the pyrite is 25% to 30% and the kaolinite clay is 70% to 75%. After years of mining and processing, hundreds of millions of tons tailings which mainly consist of kaolinite have been produced. However, the tailings have not been used effectively as yet, occupying a lot of land and causing adverse effects to the local ecological environment. What's more, it's a waste of resources [3-7].

As research shows, kaolinite being calcined and ground will be provided with high pozzolanic activity and can be used as fine cement admixture and high-performance concrete admixture [8-12]. Due to the limited kaolin resources in China, using calcined kaolinite (metakaolin) as cement admixture and concrete admixture is costly and cannot get a certain resource support. However, the main mineral of the tailings is kaolinite. Both the iron oxide and the titanium oxide which contain in the tailings have tiny effects when the tailings are used as cement admixture and concrete admixture. Therefore, the tailings can be utilized directly without being purified and processed. Presently, the cement annual output of China is more than 2.4 billion tons which accounts for 60% of the world's total cement production. From all the foregoing, using the tailings as cement admixture and concrete admixture after calcined have got a huge market demand and can obtain both economic and environmental benefit.

2. Experiments

2.1 Raw materials

The cement used was Portland cement with the strength grade of 42.5 conforming to the Chinese National Standard GB175-1999. In all cement mortar experiments, the aggregates used were standard sands. In all concrete experiments, the coarse aggregates used were natural crushed stones with the size of 4.75-13.2mm and the fine aggregates used were natural river sands with fineness module of 2.5. By X-ray fluorescence analysis, the chemical compositions of the tailings used is shown in Table 1. Figs. 1 and 2 show the X-ray diffraction analysis of the primary tailings and the tailings calcined at 800℃ for 0.5 hour and 1 hour, respectively.

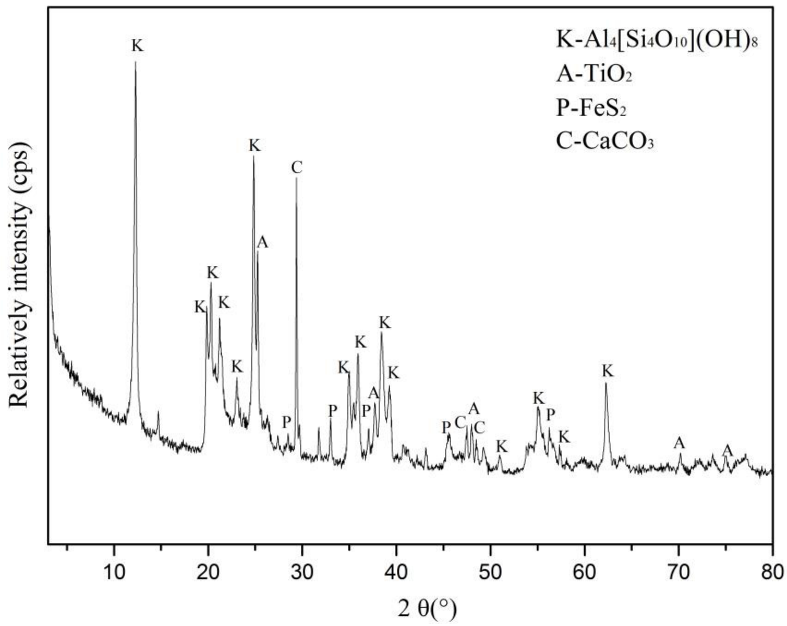


Fig. 1 XRD analysis of primary tailings.

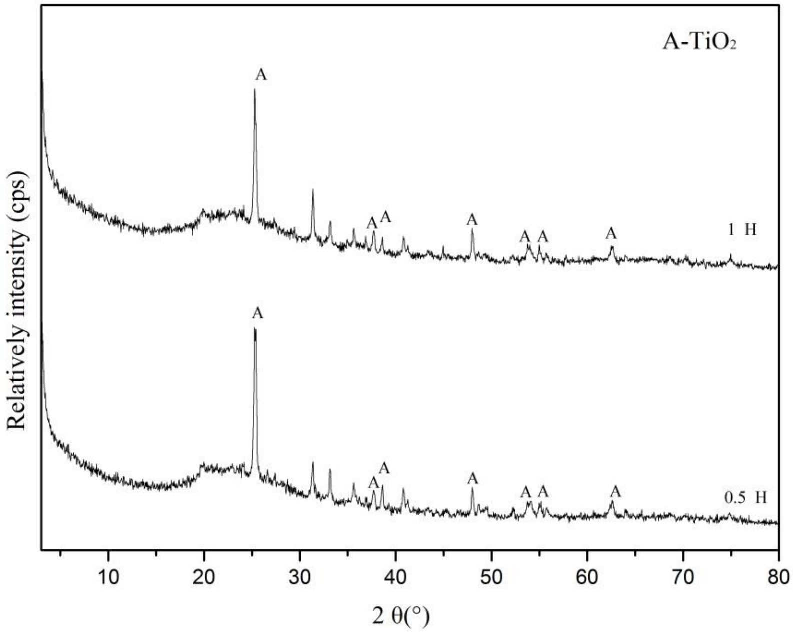


Fig. 2 XRD analysis of tailings calcined at 800℃.

Table 1 Chemical composition of the tailing(%)

Composition	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	SO_3	K_2O	MgO	ZrO_2	Na_2O
Tailing	42.79	35.36	3.19	5.98	6.22	5.41	0.21	0.22	0.17	0.03

Table 1 shows SiO_2 and Al_2O_3 are the predominant chemical compositions of the tailings and the content of K_2O and Na_2O is pretty low.

Fig. 1 shows that the tailings mainly consists of kaolinite with a small quality of anatase and pytite. Fig. 2 shows after calcined at 800℃ the kaolinite contains in the tailings will be decomposed into amorphous SiO_2 and Al_2O_3, namely metakaolin. The molecular arrangement of the metakaolin is irregular. The metakaolin is in the thermodynamic metastable state and will be provided with high pozzolanic activity after ground.

2.2 Mix proportions

All the cement mortars at different calcination temperature, different holding time or different grinding time are under the same mix proportion which is shown in Table 2.

Table 2 Mix proportions of cement mortars

Tailing replacement(by weight(%)	Compositions of cement mortar(g)			
	Cement	Processed tailing	Aggregates	Water
10	405	45	1350	225

Before being used in the concrete experiment, the tailings need calcining at 800℃ for 0.5 hour and grinding for 1.5 hours. The mix proportions of the concretes are shown in Table 3.

Table 3 Mix proportions of the concretes

Tailing replacement by weight(%)	Mix proportions of the concrete /kg.m^{-3}				
	Cement	Processed tailing	Coarse aggregates	Fine aggregates	Water
0	523	0	1153	494	230
5	497	26	1153	494	230
10	471	52	1153	494	230
20	419	104	1153	494	230
30	366	157	1153	494	230
40	314	209	1153	494	230

2.3 Test methods

2.3.1 Cement admixture experiment

The tailings were extruded as small bars with the diameter of 5mm and then dried at 105℃. The dried tailings were calcined in the muffle furnace for appropriate time at the settled temperature and cooled in the air. After being ground, the fineness of the tailings were measured with laser granulometry.

The compressive strength of the mortar samples were measured conforming to the Chinese National Standard GB/T18736-2002 and the formula of calculating the activity index was shown as follow.

$H28 = R/R0 \times 100\%$

H28—the activity index of the sample

R—the 28day's compressive strength of the test sample，

R0—the 28day's compressive strength of the reference sample

2.3.2 Concrete admixture experiment

Concrete samples of 100×100×100mm were prepared for the compressive strength test. The samples were cured under the condition of 20±1℃ and 95±5% relative humidity. At the age of 28 days, the compressive strength of the concretes were measured. .

3. Results and discussion

3.1. Influence of grinding time on the fineness of the tailings

Figs. 3 and 4 show the influence of grinding time on the fineness of the tailings at the holding time of 0.5 hour and 1.5 hours, respectively. From Figs. 3 and 4, it is evident that the calcination temperature and the holding time make minor contribution to the influence of the tailing fineness in contrast with the grinding time. Moreover, the longer the grinding time is, the tinier the fineness of the tailing will be. 90% of the tailings is less than 20μm when ground for 1 hour and 3.6μm ground for 3 hours.

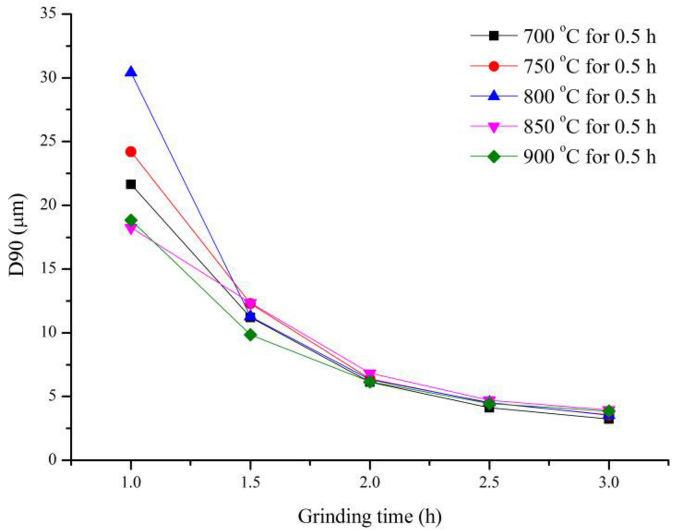


Fig. 3 Relations of grinding time to fineness（0.5 h）

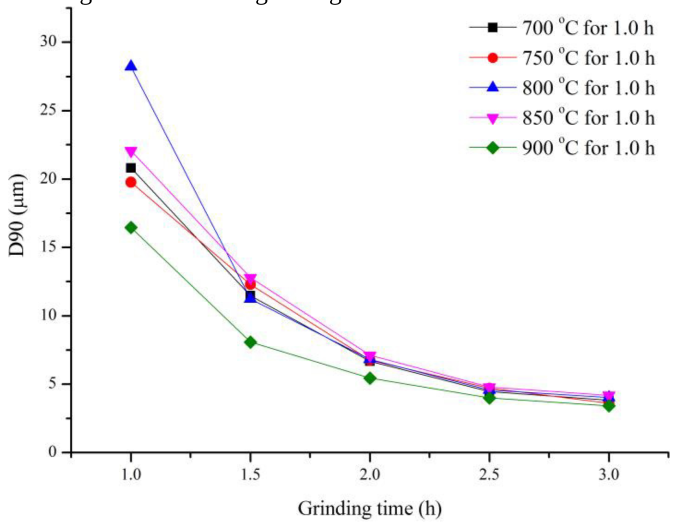


Fig. 4 Relations of grinding time to fineness（1 h）

3.2. Influencing factors of activity index

Fig. 5 and 6 show the relation of calcination temperature to the activity index under different grinding time at the holding time of 0.5 hour and 1 hour, respectively.

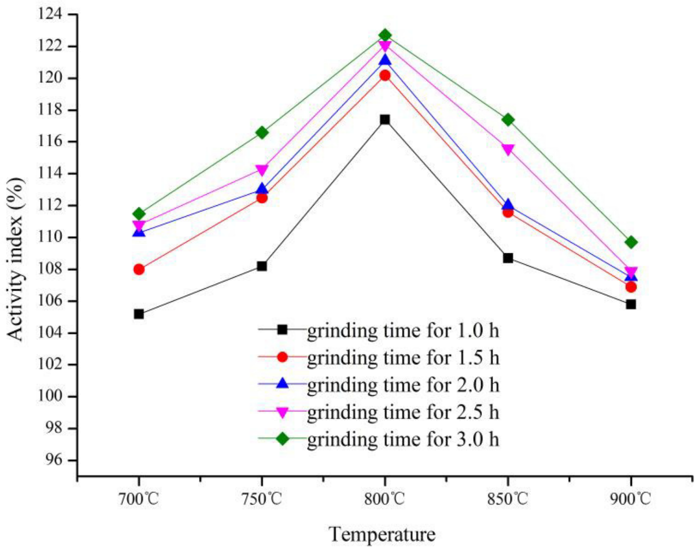


Fig. 5 Relations of calcination temperature to the activity index（0.5 h）

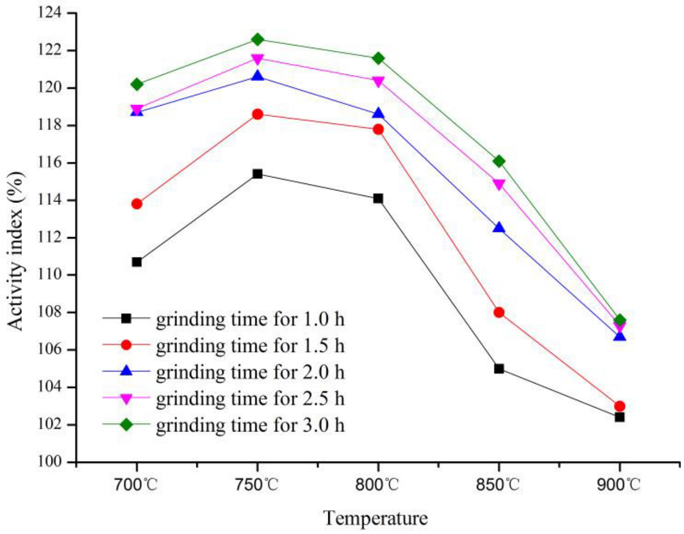


Fig. 6 Relations of calcination temperature to the activity index（1 h）

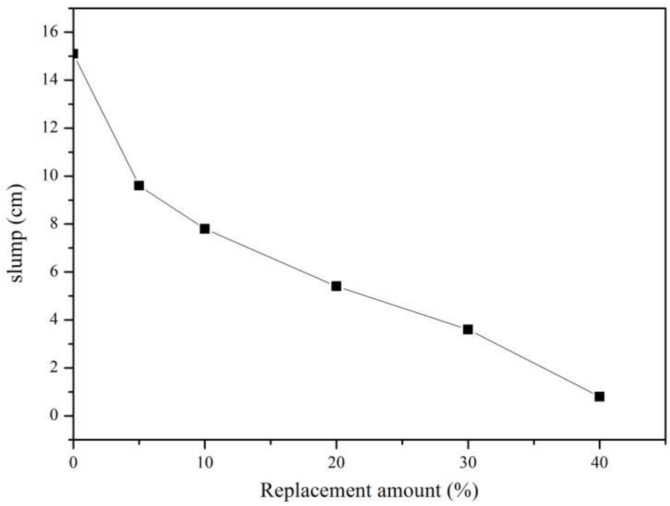
As shown in Figs. 5 and 6, the activity indexes of all the test samples are higher than the activity index of the reference sample（which is defined as 100%）. Accordingly, being calcined on appropriate temperature and ground to a certain fineness, the tailings will be provided with high pozzolanic activity. At the same holding time and grinding time and different calcination temperature, the test sample reaches the highest activity index under the conditions of both 750℃ calcining for 1 hour and 800℃ calcining for 0.5 hour. Then, it can be seen that calcination temperature and holding time have obvious effects on the cementitious activity of the tailings.

At the same calcination temperature and holding time, taking the grinding time into the only consideration, the activity index of the sample increases as the grinding time increases. The specific surface area of the tailings is increasing as the size of tailings becomes much smaller. The high specific surface area provides more active contact surface for chemical reaction. Thus, it is clear that the pozzolanic activity increases with fineness of the calcined tailings. Although the activity index increases along with the fineness of the tailing, the growth range is negligible. The activity index is 120% when ground for 1.5 hours（D90=12μm）. The activity index is 122% when ground for 3 hours（D90 =4μm）.

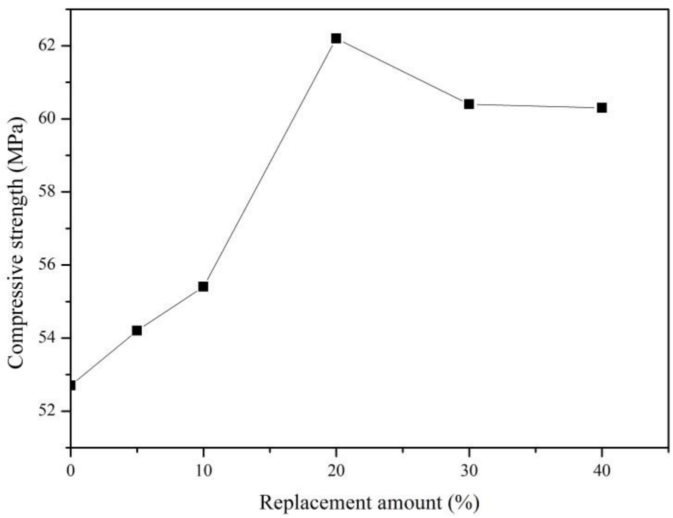
Ground 1.5 hours later (D90＜12μm）, the activity index of the samples merely gets a little increase. As a result, taking energy consumption into consideration, the optimum grinding fineness of the tailings is about 12μm.

3.3. Influence of replacement amount of the tailing on the compressive strength and slump of the concrete

The tailings are calcined at 800℃ for 0.5 hour and ground for 1.5 hours to manufacture concretes with the design strength of 50 at different replacement amount. The relation of replacement amount of the processed tailings to the slump of the concrete is shown in Fig. 7. After being cured under the condition of 20±1℃ and 95±5% relative humidity for 28 days, the compressive strength of the concrete are measured. The relation of replacement amount of the processed tailings to the compressive strength of the concrete is shown in Fig. 8.



Figs. 7 Relations of replacement amount of the tailing to the slump.



Figs. 8 Relations of replacement amount of the tailing to 28 days' Compressive strength.

Figs. 7 shows that the slump of the concrete decreases gradually as the replacement amount of the tailings increases. When the tailings replace cement for 40% by weight, the slump of the concrete is only 0.8cm which means the new mixed concrete almost loses its liquidity.

Figs. 8 shows that the 28 day's compressive strength of concrete samples with all different replacement amount of the processed tailings are higher than the 28 day's compressive strength of the pure cement concrete. Therefore, it is the second evidence for the high pozzolanic activity of the tailings after being calcined and ground. The processed tailings can be used as concrete admixture because of the high pozzolanic activity. What's more, the concrete sample will be provided with the highest compressive strength when the processed tailings replace cement for 20% by weight. As a result, taking the workability and compressive strength into consideration, the optional replacement amount of the processed tailings is 20% when used as concrete admixture.

4. Discussion on the action mechanism of the activity of metakaolin

（1）The constitution water of the kaolinite starts to decompose at 600℃ and the crystal structure is completely destroyed at 900℃. During this process, amorphous metakaolin arises and the reaction formula is shown as follow.

$$Al_4[Si_4O_{10}](OH)_8 \xrightarrow{600-900℃} SiO_2 + Al_2O_3 + H_2O$$

The atomic arrangement of the metakaolin created from the kaolinite when calcined from 600℃ to 900℃ is irregular and the metakaolin presents the thermodynamic metastable state. Meanwhile, owing to the calcination, there are plentiful broken chemical bonds in the metakaolin and the specific surface area increases significantly which will generate large amount of surface energy. Consequently, the metakaolin is provided with high pozzolanic activity. SiO_2 and Al_2O_3 contained within the metakaolin will react with the calcium hydroxide which is the hydration products of cement. The reaction product is the C-S-H gel of $C_3S_2H_3$, C_4AH_{13} and C_2ASH_8 for which will improve the compressive strength and performance of the concrete. The formation of these hydration products largely depends on the weight ratio of AS_2/CH. The reaction formulas are listed as follow.

$$AS_2 / CH = 0.5, \quad AS_2 + 6CH + 9H \longrightarrow C_4AH_{13} + 2CSH$$

$$AS_2 / CH = 0.6, \quad AS_2 + 5CH + 3H \longrightarrow C_3AH_6 + 2CSH$$

$$AS_2 / CH = 1.0, \quad AS_2 + 3CH + 6H \longrightarrow C_2AH_8 + CSH$$

（2）Besides pozzolanic activity, the ground metakaolin is provided with filling effect of aggregate as well. Research shows, the hardened cement paste is porous and there are blocky and flaky $Ca(OH)_2$ crystals in the pores. The ground metakaolin will reduce the porosity of the concrete. As a result, the growing space for hydration products will reduce and the concrete structure becomes more voidless. Obvious $Ca(OH)_2$ crystals in the concrete disappear and a large amount of clustered hydration products which is well-distributed produce. Accordingly, the mechanical properties of the concrete improves. From the foregoing, the advantages of using fine metakaolin to replace cement as admixture are reducing the porosity, modifying the pore structure, improving compressive strength, impermeability and durability of the concrete.

5. Conclusions

（1）The predominant chemical compositions of the tailing are SiO_2 and Al_2O_3., and the content of K_2O and Na_2O is pretty low. The main mineral of the tailings is kaolinite, and the anatase is slender.

（2）When used as cement admixture, the sample will be provided with the hightest activity index of 122% at the condition of both 750℃ calcining for 1 hour and 800℃ calcining for 0.5 hour.

（3）The tinier the fineness is, the higher the pozzolanic activity of the tailing will be. However, as 90% the tailings' fineness is less than 12μm, the growth range of the activity index is negligible. By overall consideration, the optimal grinding fineness of the tailings is 12μm.

（4）Being used as concrete admixture, the optimal amount of the tailing is 20% of cement by weight. The concrete still has good workability at this amount of tailing.

（5）The tailings will be provided with high pozzolanic activity after being processed under proper conditions. It can be used as fine cement admixture and high-performance concrete admixture, which turns out to be the effective way to using the tailings.

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